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DISPLACEMENT REACTIONS.[1] XI. QUANTITATIVE CORRELATION OF RATES

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This paper discusses and compares quantitative correlations of
rates which are in the form of linear free-energy relationships. Two new
correlations of rates of solvolysis are proposed. A common measure of
goodness of fit is proposed, and calculated for typical applications of
the Bronsted catalysis law, the Hammett equation, the Grunwald-Winstein
equation, and our new correlations.

Many of the quantitative correlations of the effect of structure

on the reactivity of organic compounds are effectively linear free-energy

relationships, because they are linear equations involving logarithms of rate

constants ($\underline{k}$) or equilibrium constants ($\underline{K}$) or both, and these logarithms in

turn are linear functions of the corresponding free energies.[2]

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw Hill Book Co., Inc.,
New York, N. Y., 1940, Chap. VII.

$$\log \underline{k} = -\frac{\Delta F^*}{2.303\ \underline{RT}} + \log\left(\frac{\underline{RT}}{\underline{Nh}}\right)$$

$$\log \underline{K} = -\frac{\Delta F^{\circ}}{2.303\ \underline{RT}}$$

The fields of application and limitations of the most important ones are

summarized briefly below.

The Brönsted Catalysis Law. — The first linear free-energy

relationship was the Brönsted catalysis law,[3] which correlates the rate

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(3) J. N. Brönsted and E. A. Guggenheim, J. Am. Chem. Soc., 49, 2554 (1927); J. N. Brönsted, Chem. Rev., 5, 312 (1928); L. P. Hammett, loc. cit., pp. 222-228.

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of a base- or an acid-catalyzed reaction with the strength of the catalyzing

base or acid. It has the form

$$\log k = \beta \log K + C \tag{1}$$

where log is the decimal logarithm, k is the rate constant with any base

(or acid) in any medium at any temperature, K is the basic (or acidic)

ionization constant of the base (or acid), usually taken in water at 25°,

and β and C are constants characteristic of the type of reaction (reactants,

medium and temperature). Values of β most commonly range from 0.3 to 0.9.

The Brönsted law implies that the free energy of activation of a

base- or an acid-catalyzed reaction is only a fraction of the free energy of

ionization of the base or acid. It is possible that β measures the fraction

of completion of the proton transfer at the transition state.

For a given reaction the best values of β and C for carboxylate

anions (determined by the method of least squares) may be slightly different

than the best values for phenolate ions or amines, and hydroxide ion and

water may also show significant deviations. All these deviations are smaller

if one correlates the rates in one reaction (e.g., mutarotation of glucose)

with the rates in a similar reaction (e.g., enolization of acetone or

decomposition of nitramide) for the same bases.[4]

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(4) H. L. Pfluger, J. Am. Chem. Soc., 60, 1513 (1938).

$$\log k_B = \gamma \log k'_B + C'$$

The Hammett Equation.- The next linear free-energy relationship to

be tested was the Hammett equation[5]

$$\log\left(\frac{k}{k^\circ}\right) = \rho\sigma \qquad\qquad (2)$$

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(5) L. P. Hammett, loc. cit., pp. 184-198; Chem. Rev., 17, 125 (1935); Trans. Faraday Soc., 34, 156 (1938).

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where $\underline{k}$ is either a rate or an equilibrium constant for a $\underline{m}$- or $\underline{p}$- substituted benzene derivative, $\underline{k}^\circ$ is the corresponding constant for the unsubstituted benzene derivative, σ depends on only the substituent (0.00 for H) and ρ depends on only the reaction (reactants, medium, temperature). To determine σ values, ρ was taken as + 1.000 for the ionization constants ($\underline{K}$) of benzoic acids in water at 25°. Hammett tabulated σ values for 43 substituents and ρ values for 52 reactions. The substituent parameter (σ) is negative for electron donating substituents, positive for electron attracting substituents. The $\underline{m}$- σ value for a substituent is a rough measure of its inductive effect, whereas its $\underline{p}$- σ value roughly measures the sum of its resonance and inductive effect.

The factors determining the sign and magnitude of ρ have been discussed recently.[6] Usually ρ is found to be quite independent of the

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(6) C. G. Swain and W. P. Langsdorf, Jr., J. Am. Chem. Soc., 73, 2813 (1951); C. T. Hathaway, Ph.D. Thesis, M.I.T., July, 1953; C. G. Swain, W. H. Stockmayer and J. T. Clarke, J. Am. Chem. Soc., 72, 5426 (1950).

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substituent within the experimental error. However there are many reactions of benzyl and benzoyl halides where a plot of log $\underline{k}$ vs. σ has real positive curvature, and some plots even have minima. This can be handled either by assigning special values of σ for such reactions or by considering ρ as a function of the polarizability of the compound undergoing displacement, the substituent, and its location ($\underline{m}$- or $\underline{p}$-).

Taft[7a] found a way to modify the Hammett equation to make it

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(7) (a) R. W. Taft, Jr., J. Am. Chem. Soc., 74, 2729, 3120 (1952); 4231 (1953); (b) C. K. Ingold, J. Chem. Soc., 1032 (1930).

applicable to ester formation and ester hydrolysis of aliphatic and o-substituted benzoic esters by use of the equations

$$\log (k/k^\circ) = \rho^* \sigma^* + E_s \quad \text{for any ester formation or hydrolysis}$$

$$2.48 \, \sigma^* = \log (k/k^\circ)_B - \log (k/k^\circ)_A \quad \text{for a standard ester hydrolysis}$$

where σ^* is a measure of the polarity of a substituent R, E_s is a measure of the steric effect of R in RCOOH or its esters, k and k° are rate constants with any substituent and with a standard substituent, and B and A refer to base- and acid-catalyzed reactions respectively. The fundamental assumption on which this method for separating polar from steric effects rests is that the steric effects are the same in base- and acid-catalyzed ester reactions.[7b]

Polar substituent constants (σ^*) were tabulated for 34 aliphatic substituents (R) defining $\sigma^* = 0$ for R = CH_3, and for 7 o-substituted phenyls using a different scale where $\sigma^* = 0$ for unsubstituted phenyl. Steric constants (E_s) were tabulated for 39 aliphatic substituents and 8 o-substituted phenyls.

The polar substituent constants (σ^*) so obtained proved to be linear functions of (1) the free energy of ionization of the corresponding acids RCOOH, (2) the free energy of activation of corresponding 3-alkylpyridines RC_5H_4N with methyl iodide or of alkyl chlorides RCl with sodium, and (3) certain physical parameters such as dipole moments of RCl and heats of dissociation of amine (RNH_2) - trimethylboron addition complexes. Thus any one of these quantities may be considered a direct measure of polar effects under conditions where steric and resonance factors are essentially constant.

Jaffé[8] pointed out that the change in log k caused by introducing a

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(8) H. H. Jaffé, Science, 118, 246 (1953).

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4- or 5-substituent in a phenyl compound is generally equal within experimental error to the change in log k when a constant ortho (2-) substituent is also present (resulting in 2, x-disubstitution, with x = 4 or 5).

Consequently,

$$\log\left(\frac{k_{a,x}}{k^\circ}\right) \;-\; \log\left(\frac{k_a}{k^\circ}\right) \;=\; \log\left(\frac{k_x}{k^\circ}\right)$$

$$=\; \rho\,\sigma_x$$

Thus the kinetic energy or entropy terms which prevent correlation of the effect of ortho substituents are effectively cancelled out by taking the difference of logs since the troublesome terms are common to both of the logs.

The Grunwald-Winstein Correlation of Solvolysis Rates.- Grunwald and Winstein[9] tested another linear free-energy relationship

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(9) E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948); S. Winstein, E. Grunwald and H. W. Jones, ibid., 73, 2700 (1951),

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$$\log (k/k^\circ) = m\,Y \tag{3}$$

where k is the first-order rate constant for solvolysis in any medium, k° is the corresponding constant in 80% ethanol, m depends on only the compound undergoing solvolysis, and Y depends on only the solvent. To determine Y values, m was taken as + 1.00 for t-butyl chloride at 25°. This equation then correlates rates of hydrolysis, alcoholysis, acetolysis and formolysis of tertiary aliphatic halides, pinacolyl brosylate (α-methylneopentyl p-bromobenzenesulfonate), trans-2-bromocyclohexyl brosylate and several other compounds very well. Compounds which correlate are classified as "limiting" in mechanism. The fit is poorer (unless different Y values are used or unless acetone-water mixtures and carboxylic acids are excluded) for i-propyl p-bromobenzenesulfonate and benzhydryl chloride; and especially poor for p-nitrobenzoyl chloride, n-butyl bromide and trityl fluoride (see last section of measure of fit). The lack of correlation with trityl fluoride, which is relatively more sensitive to acidic solvents than t-butyl chloride and gives a stabler ion, casts doubt on the classification of t-butyl chloride as "limiting."

An attempt was made[10] to base one $\underline{Y}$ scale on trityl fluoride

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(10) C. G. Swain and R. B. Mosely, <u>J. Am. Chem. Soc.</u>, <u>76</u>, 000 (1954); cf.
S. Winstein, E. Grunwald and H. W. Jones, <u>ibid.</u>, <u>73</u>, 2704 (1951).

($\underline{Y}_A$) and another on $\underline{n}$-butyl bromide ($\underline{Y}_B$), and then to express any first-order rate constant for a compound of intermediate structure as the sum of two first-order rate constants, as if there were two discrete mechanisms, A and B.

$$\underline{k} = \underline{k}_A + \underline{k}_B$$

$$\log (\underline{k}_A / \underline{k}_{A\circ}) = \underline{m}_A \underline{Y}_A \qquad (3a)$$

$$\log (\underline{k}_B / \underline{k}_{B\circ}) = \underline{m}_B \underline{Y}_B \qquad (3b)$$

Even though $\underline{m}_A$ and $\underline{m}_B$ are independently adjustable parameters, this completely failed to correlate the rates of $\underline{t}$-butyl chloride.

Although this proves that $\underline{t}$-butyl chloride is not reacting by a <u>mixture</u> of mechanisms capable of being represented separately by equations 3a and 3b, it does not exclude reaction by an <u>intermediate</u> or hybrid mechanism; and in fact the behavior of $\underline{t}$-butyl chloride is in every way intermediate between that of $\underline{n}$-butyl bromide and trityl fluoride. One way to see this is with plots of log $\underline{k}$ for $\underline{n}$-butyl bromide and trityl fluoride vs. $\underline{Y}$ values based on $\underline{t}$-butyl chloride. Although at first glance they appear to be scatter plots, closer inspection reveals that whereas for $\underline{n}$-butyl bromide the acidic solvents are slower than expected from the behavior of the alcohol-water mixtures they are faster than expected by about the same factor for trityl fluoride. The reverse is true for acetone-water mixtures. In fact $\underline{t}$-butyl chloride is approximately halfway between $\underline{n}$-butyl bromide and trityl fluoride in behavior, which makes it hard to believe that its mechanism is "limiting" in type.

A further reason for concern with equation 3 is the fact that its application to mixed solvents is theoretically unsound: if it held rigorously

for pure solvents it would have to fail for ideal binary solvent mixtures for all compounds for which $\underline{m}$ was not equal to one. This follows because one electrophilic component of a mixture should be relatively more important than another by a varying factor (resulting in a different average $\underline{Y}$ for the mixture), depending on the selectivity ($\underline{m}$) of the substrate. The $\underline{Y}$ for an ideal binary mixture of C and D in terms of the $\underline{Y}$'s and mole fractions (x) for the pure components should be

$$\underline{Y} = x_C 10^{\underline{m}\,\underline{Y}_C} + x_D 10^{\underline{m}\,\underline{Y}_D} \tag{4}$$

and thus should depend on $\underline{m}$ as well as on $\underline{Y}_C$ and $\underline{Y}_D$. Therefore it might seem preferable to measure $\underline{Y}$ values only for pure solvents, and use equation 4 to calculate $\underline{Y}$ for mixtures. Unfortunately the binary mixtures used in practice are so non-ideal that 4 does not adequately describe the variation in rate with composition even for a single compound.[11] Consequently

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(11) M. (Inka) Allen, S.M. Thesis, M.I.T., August, 1953.

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the assumption of Grunwald and Winstein that $\underline{Y}$ of a binary mixture is independent of $\underline{m}$ in fact gives a much better fit (because it has more experimentally determined parameters and hence more flexibility) than the assumption of ideal behavior embodied in equation 4.

In this laboratory, we have focused attention on the effect on the rate of simple polar displacement reactions caused by changing the "nucleophilic" reagent or the "electrophilic" reagent. The following section defines these terms and presents the physical picture on which our correlations are based.

The Nature of Polar Displacement Reactions.- The commonest chemical reaction for an uncharged substrate (S) appears to be a displacement involving both a nucleophilic reagent (N) and an electrophilic reagent (E) attacking in, or prior to, the slowest step on the way to the products.

Just as there is no pure covalent bond and all real bonds have a

certain degree of ionic character, likewise nucleophilic and electrophilic

attack will vary from largely covalent interactions to almost purely

electrostatic solvation. To avoid the need for drawing an arbitrary dividing

line, we include all these behaviors in our definition: a nucelophilic (or

electrophilic) reagent is an electron pair donor (or acceptor) with an

inherent tendency to form a partly covalent bond rapidly.[12] We use the term

(12) Note that this definition is nevertheless narrower than the one given
by C. K. Ingold (J. Chem. Soc., 1120 (1933); "Structure and Mechanism in
Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 200) which
does not mention electron pairs, bonding, or rate. He gave ferro- and
ferri-cyanide ions as examples of nucleophilic and electrophilic reagents
respectively.

basic (or acidic) to refer to equilibrium instead of rate.

Rate data may be used to study the structure of the transition

state. If faster rates are obtained with the most polar solvating reagents,

the transition state has more charge separation than the initial reactants.

The effect of m- and p-substituents reveals whether bond making or bond

breaking is the more complete at the transition state.[6] The size of the

isotope effect of α-hydrogens may indicate the magnitude of the positive

charge on a central carbon at the transition state.[13]

(13) E. S. Lewis and C. E. Boozer, J. Am. Chem. Soc., 74, 6306 (1952);
V. J. Shiner, Jr., ibid., 74, 5285 (1952), 75, 2925 (1953).

Intermediates are harder to study than transition states, and are

rigorously established experimentally only under especially favorable

circumstances, e.g., by successful competition experiments in which (1)

the product but not the rate is drastically changed by addition of a

sufficiently nucleophilic reagent or (2) the rate but not the final percent

reaction is cut down significantly by adding a common product ion (the

"mass effect") or (3) the substrate rearranges or racemizes at a rate

comparable to its rate of solvolysis or rate of over-all displacement by

external nucleophilic reagents ("internal return").[14]

(14) W. G. Young, S. Winstein and H. L. Goering, J. Am. Chem. Soc., 73, 1958 (1951); S. Winstein et al., ibid., 74, 1154, 2165, 2171, 5585 (1952).

In rare cases an intermediate will accumulate enough to be detectable analytically. For example absorption at 4980 $\overset{\circ}{A}$ due to the carbonium ion intermediate rises for 55 seconds and then falls more slowly in the reaction of 0.0022 M. tris-p-methoxytrityl chloride with 0.28 M. pyrrole in dry benzene at 25°.[15] The maximum concentration of carbonium ion

(15) L. E. Kaiser, Ph.D. Thesis, M.I.T.

is 3.4×10^{-6} M assuming the same extinction coefficient for the carbonium ion in benzene as in 100% sulfuric acid. Other examples of accumulating intermediates are the cyclic immonium ions in the reactions of tertiary β-chloroethylamines (nitrogen mustards) in aqueous solution,[16] which accumulate

(16) P. D. Bartlett, J. W. Davis, S. D. Ross and C. G. Swain, J. Am. Chem. Soc., 69, 2971, 2977 (1947); 71, 1415 (1949).

enough to be titrated volumetrically (by difference in $AgNO_3$ and NaOH titers, or by rapid titration with $Na_2S_2O_3$) or to be isolated by precipitation as picrylsulfonates.

A unified view would hold that intermediates of minor stability are quite common, occurring even in the uncatalyzed hydrolysis of methyl halides, so that there are only quantitative differences between methyl and triphenylmethyl compounds. However, it is difficult to obtain any evidence for intermediates which are close in structure to a tight transition state, i.e., one with all bonds relatively highly covalent. When the transition state is loose, i.e., when the bonds to the atom undergoing displacement are more ionic in character and longer, neighboring intermediates are more often detected because such a sizeable activation energy may accompany further

bonding that other reactions may compete successfully for an intermediate.
It is a general rule that the greater the change in covalent bonding involved
in given step, the slower is its rate.

The Kinetics of Polar Displacement Reactions.- The total rate of
reaction of an uncharged substrate S in solution may often be approximated by

$$ - d[S]/dt = \sum_{ij} k_{ij} [N_i] [S] [E_j] \qquad (5) $$

where $[N_i]$ and $[E_j]$ represent the concentrations of free nucleophilic
reagents and electrophilic reagents (often less than the stoichiometric
concentrations because of association or complexing). Then any particular
term in the rate expression (on the right side of equation 1) is third order,
second order or first order depending on whether neither, either or each of
the reagents N and E involved in that term is in large excess (e.g., is the
solvent or part of the solvent). Usually any particular term can be made to
predominate strongly over all others by proper choice of concentrations and
other reaction conditions, and one generally tries to design experiments to
accomplish this when measuring a particular k_{ij}; where this is not possible,
the more general summation must be used.

Equation 5 is most obviously correct for concerted mechanisms,
i.e., ones which may be represented by

$$ N + S + E \xrightarrow[\text{slow}]{k} \text{Products} $$

or by
$$ N + S + E \xrightarrow[\text{slow}]{k} S' $$

$$ S' \xrightarrow{\text{any speed}} N + S + E $$

$$ S' \xrightarrow{\text{fast}} \text{Products} $$
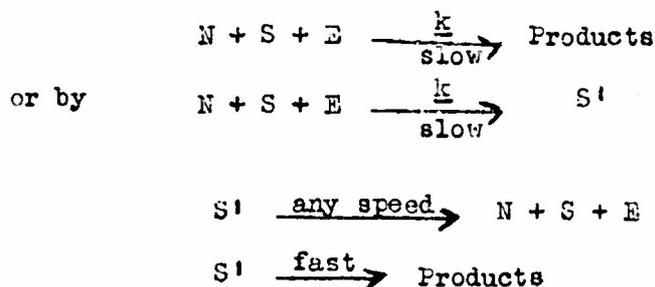
Examples of these may include reaction of pyridine with methyl bromide
catalyzed by phenol or mercuric ion in benzene solution,[17] mutarotation of

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(17) C. G. Swain and R. W. Eddy, J. Am. Chem. Soc., 70, 2989 (1948).

tetramethylglucose by pyridine and phenol in benzene solution,[18] enolization

(18)   C. G. Swain and J. F. Brown, Jr., *ibid.*, 74, 2534, 2538, 2691 (1952).

of acetone by acetate ion and acetic acid in water solution (third-order

term),[19] reaction of iodide ion with epichlorohydrin catalyzed by acetic

(19) H.M.Dawson and E.Spivey, *J. Chem. Soc.*, 2180 (1930).

acid in water solution,[20] and cleavage of organosilicon compounds in water

(20)   C. G. Swain, *J. Am. Chem. Soc.*, 74, 4108 (1952).

solution.[21]

(21)   F. P. Price, *ibid.*, 69, 2600 (1947).

Equation 5 should also hold for mechanisms involving **successive** attacks,

$$S + E \underset{fast}{\overset{K}{\rightleftharpoons}} S'$$

$$N + S' \xrightarrow[slow]{k} \text{Products}$$

$$\text{or} \quad N + S \underset{}{\overset{K}{\rightleftharpoons}} S'$$

$$S' + E \xrightarrow[slow]{k} \text{Products}$$
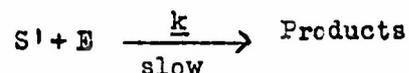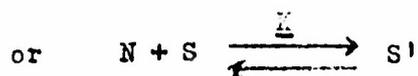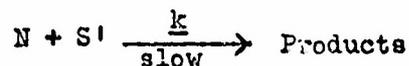
provided that the equilibrium constants ($\underline{K}$) are small enough so that $[S'] \ll [S]$ under all the conditions used. Reactions such as methanolysis of trityl chloride in benzene solution,[22] most reactions in water solution (e.g.

(22)   C. G. Swain, *ibid.*, 70,1119 (1948); 72, 2794 (1950).

hydrolysis of halides or mutarotation of glucose), and decomposition of mesitoic acid in sulfuric acid (water required)[23] probably involve either a

(23)   W. M. Schubert, *ibid.*, 71, 2639 (1949).

concerted mechanism or successive attacks, but it is not yet certain which in any of these cases.

Equation 5, which contains the factor [N], may be in error for decomposition of trioxane or formic acid in sulfuric acid-water mixtures or for any other reactions where log (rate)/[S] shows a linear dependence on Hammett's acidity function, H_o, with a slope of 1.0. In such cases either (1) no nucleophilic reagent is involved in the transition state or (2) the nucleophilic reagent involved is one previously associated with the substrate in the ground state or (3) the substrate discriminates very little among different nucleophilic reagents, and the solvent (because of its higher concentration) is the only species significantly involved in nucleophilic attack.

Equation 5 is expected to fail whenever such strong nucleophilic or electrophilic reagents are used that most of the substrate is complexed in the ground state (i.e., $[S'] > [S]$, $\underline{K} > 1$), or whenever S itself is an anion or a cation. It will also fail for four-center reactions (e.g. $H_2 + I_2$).

$\underline{\text{Nucleophilic and Electrophilic Constants}}$.- When equation 5 applies, it is often useful to compare the observed rate constants, $\underline{k}_{ij}$, hereafter abbreviated simply as $\underline{k}$, with the corresponding observed rate constant, $\underline{k}^o$, for reaction with a standard nucleophilic reagent, N^o, and a standard electrophilic reagent, E^o, using the same solvent, inert salts, pressure and temperature. The quantity log $(\underline{k}/\underline{k}^o)$ is then proportional to the difference in free energy of activation $\Delta\Delta F^*$ of two reactions

$$N + S + E \xrightarrow{\ \underline{k}\ } \text{Products}$$

$$N^o + S + E^o \xrightarrow{\ \underline{k}^o\ } \text{Different products.}$$
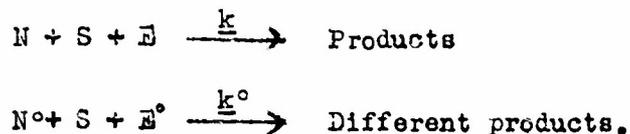
As indicated above, it is not important for the comparison of rates whether either of these reactions symbolizes a concerted mechanism or two successive steps with an intermediate (S') in low concentration, or some mixture of these mechanisms. Clearly the difference in free energy of activation is

partly due to the change in N and partly due to the change in E. Therefore for a standard substrate S° we may write

$$\log (k/k_o) = \underline{n} + \underline{e}$$

where $\underline{n}$ depends on N only (equals 0.00 for N°) and $\underline{e}$ depends on E only (equals 0.00 for E°). Another substrate S may be more selective or less selective among nucleophilic and electrophilic reagents than S°. Hence for any other substrate

$$\log (k/k°) = \underline{s}\,\underline{n} + \underline{s}'\underline{e} \tag{6}$$

where $\underline{s}$ measures its discrimination among nucleophilic reagents and $\underline{s}'$ measures its discrimination among electrophilic reagents. The constants $\underline{s}$ and $\underline{s}'$ both depend on S only, but are independent of one another except that both equal 1.00 for S°. The term $\underline{s}\,\underline{n}$ measures the difference in nucleophilic driving force between the two reactions and $\underline{s}'\underline{e}$ measures the difference in electrophilic driving force. The quantities 2.303 $\underline{RT}$ $\underline{s}\underline{n}$ and 2.303 $\underline{RT}$ $\underline{s}'\underline{e}$ have units of kcal.

Inherent in equation 6 is the assumption that the ratio of rates with N and N° is independent of what electrophilic reagent is acting, and that similarly the relative reactivities of electrophilic reagents are independent of N. Inherent also is the assumption that $\underline{s}$ and $\underline{s}'$ are true constants, independent of the choice of nucleophilic or electrophilic reagents. These assumptions have the maximum chance of being correct when (1) equation 5 applies, (2) solvent, inert salts, temperature and pressure are approximately consatnt in the experiments compared, (3) the displacements compared are all simple displacements on a single kind of atom (e.g., a saturated carbon atom), and (4) charged nucleophilic and electrophilic reagents (which are more likely to influence each other's reactivity) are excluded from the comparisons.

Only certain corollaries of equation 6 have been tested thus far. One of these arises when the electrophilic reagent is held constant, as for

example, when water is the solvent and acts as the only important electrophilic

reagent. Since one may then set e = 0.00 for E_o = H_2O, equation 6 reduces to

$$\log k/k^\circ = s\,n \ . \tag{7}$$

Here k and k° are both second-order rate constants. This corollary was

tested[24] using water, acetate ion, chloride ion, aniline, hydroxide ion,

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(24) O. G. Swain and C. B. Scott, ibid., 75, 141 (1953).

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thiosulfate ion and other nucleophilic reagents as N, and esters, ethylene

oxides, and alkyl and acyl halides as S. In all these displacements on

carbon, one constant set of n values appeared to suffice, and each substrate

could be characterized by a single s value.

Although it was not possible to correlate displacements on hydrogen

with the same set of n values, a different set of n values correlated

displacements on hydrogen with one another. A satisfactory set for

displacements on hydrogen is n = $\log (K_B/K_B^\circ)$ where K_B and K_B° are the basic

ionization constants of N and N° in water at 25°. This substitution reduces

equation 7 to the Brönsted catalysis law

$$\log (k/k^\circ) = \beta \log (K_B/K_B^\circ).$$

Still another set of n values is needed to correlate displacements

in phosphorus[25] or displacements on tin. Our data for displacements on an

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(25) I. Dostrovsky and M. Halmann, J. Chem. Soc., 508 (1953).

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unsaturated carbon atom (benzoyl chloride) were extremely limited and it

is very likely that sulfur anions will also prove abnormally weak

nucleophilic reagents in displacements on unsaturated carbon. Also the

n scales will probably be different in absolute ethanol or other solvents than

in water. However, it is our hope that after enough sets of n values are

collected, each working over a limited range of structure, it may prove

possible to express any set as a linear combination of two more fundamental

sets, with only one parameter (a relative weighting factor for the two sets) to allow for variations in the n scale (due to differences in charge, electronegativity, polarizability, and bond strength) from displacements on one atom to displacements on another, or from one solvent to another.

A Four-Parameter Correlation of Solvolysis Rates.- Equation 6 has been applied more recently to correlating rates of solvolysis.[26] Unlike the

(26) R. B. Mosely, Ph.D. Thesis, M.I.T., July, 1952; D. E. Bown, Ph.D. Thesis, M.I.T., April, 1953; Abstracts of 13th A.C.S. Organic Symposium, Ann Arbor, Michigan, June 17, 1953, pp. 63-69.

previous applications, the solvent is not kept constant in these comparisons of rates. For this reason we prefer to change the symbols to

$$\log (k/k^\circ) = c_1 d_1 + c_2 d_2 \tag{8}$$

where k, k° = first-order rate constants in any medium and in the standard medium

c_1, c_2 = parameters characteristic of compound solvolyzing (1.00 for C°)

d_1, d_2 = parameters characteristic of medium (0.00 for D°)

in order to avoid any implication that the solvent parameters are accurate measures of nucleophilic and electrophilic reactivity of the solvent when equation 6 is applied in this manner. A possible approach to obtaining true values of s, n, s' and e would involve diluting each of the solvents with an inert low-dielectric medium so that the experimental $\log (k/k^\circ)$ values could be interpolated to a constant dielectric constant for use in equation 6. We have not done this, but would expect the parameters to have much more obvious and simple physical significance if such a correction were made.

The results from applying equation 8 to kinetic data on solvolysis are given in the next paper (XII) of this series.[27] The fit is good even

(27) C. G. Swain, R. B. Mosely and D. E. Bown, J. Am. Chem. Soc., 76, 0000 (1954).

over the large range of structural variation including benzoyl, methyl and triphenylmethyl compounds in water, alcohols, acetic acid and formic acid.

A Special Two-Parameter Correlation of Solvolysis Rates.- A different approach to the correlation of rates of solvolysis is embodied in equation 9

$$\log (k/k^\circ)_A - \log (k/k^\circ)_{A^\circ} = a\ b \tag{9}$$

where k the rate constant for solvolysis in any solvent, k° is the same in a standard solvent (80% ethanol-20% water), A refers to any organic chloride or bromide, A° to a standard compound (methyl bromide), a is a constant depending only on the compound, and b is a constant depending only on the solvent.[28,29] By using a quantity $(\log k/k^\circ)_A - \log (k/k^\circ)_{A^\circ})$ proportional

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(28) C. G. Swain and D. C. Dittmer, ibid., 75, 4627 (1953).

(29) D. C. Dittmer, Ph.D. Thesis, M.I.T., September, 1953.

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to a $\Delta\Delta\Delta F^*$, all effects common either to k and k° or to A and A° are cancelled out. What is left is only a factor a, which appears to be dependent primarily on electron supply to the central carbon, and a factor b, which appears to be dependent primarily on acidity of the solvent and dielectric constant. This equation is limited to simple displacements of similar leaving groups (e.g., chlorides, or chlorides and bromides) from similar sites (e.g., carbon atoms). Nevertheless it is successful in correlating solvolysis of compounds as diverse   as t-butyl chloride, n-butyl bromide and p-nitrobenzoyl chloride in solvents as diverse as n-butylamine, methanol and anhydrous formic acid. Thus its field of application is much wider than that of equation 3 and comparable to that of the four-parameter equation 8.

It is possible that equation 9 approximates

$$\frac{(\Delta E_p^* - \Delta E_p^{*o})_A - (\Delta E_p^* - \Delta E_p^{*o})_{A^o}}{2.303\ \underline{R}\ \underline{T}} = \frac{\Delta\Delta\Delta E_p^*}{2.303\ \underline{R}\ \underline{T}}$$

where ΔE_p^* is the difference in potential energy between ground state and transition state in any solvent, and superscript zeros indicate the same for the standard solvent. This would be true if both $\Delta E_z^* - \Delta E_z^{*o}$, where E_z is the zero-point vibrational energy, and $2.303\ \underline{R}\ \underline{T} \log (Q^*Q^o/QQ^{*o})$, where Q's are partition functions, were the same for any A under consideration as for A°.[29,30]

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(30) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 118.

This equation is discussed in more detail in paper XIII[31] of this

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(31) C. G. Swain, D. C. Dittmer and L. E. Kaiser, *J. Am. Chem. Soc.*, 76, 0000 (1954).

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series.

A Measure of Goodness of Fit.- In order to compare the goodness of fit to the experimental data obtained with different quantitative correlations of rate or equilibrium constants, it is convenient to have an objective measure of fit which will be applicable to them all. This measure should consider not only the absolute errors in the calculations but also the range of the data, since an average error of a factor of 1.1 is poor if the observed data vary by only a factor of 1.2 yet an average error of a factor of 2 may be an excellent fit if the experimental data being correlated vary more of less uniformly over a range of 10^6.

A measure of fit which (1) is applicable to any correlation of rate or equilibrium constants, (2) weights all the errors and all the data equally, and (3) is simple to apply is ϕ(Phi)

$$\phi = \left(1 - \frac{\xi}{\theta}\right) 100\%$$

where $\underline{\epsilon}$ (epsilon) is the average deviation of observed from calculated logarithms (a measure of absolute error), and $\underline{\theta}$ (theta) is the average deviation of observed logarithms from their own mean (a scale factor indicating the range of the data).

$$\underline{\epsilon} = \frac{1}{\underline{n}} \sum_{\underline{n}} \left(\left| \log \underline{q}_{obs.} - \log \underline{q}_{calc.} \right| \right)$$

$$\underline{\theta} = \frac{1}{\underline{n}} \sum_{\underline{n}} \left(\left| \log \underline{q}_{obs.} - \frac{1}{\underline{n}} \sum_{\underline{n}} \log \underline{q}_{obs.} \right| \right)$$

Here $\underline{n}$ is the number of points for which $\underline{\epsilon}$ can differ from zero and for which $\underline{q}$ was observed, and $\underline{q}$ may be a rate constant ($\underline{k}$), an equilibrium constant ($\underline{K}$) or a ratio of constants (e.g., $\underline{k}/\underline{k}°$, where $\underline{k}°$ is the value of $\underline{k}$ under specified standard conditions). Values of $\underline{\Phi}$ extend from +100% for perfect correlation ($\underline{\epsilon}$ =o) to small or even negative values when there is serious scatter. Values of $\underline{\Phi}$ from 80 to 100% are designated arbitrarily as "excellent," 50-80%, "good," 20-50%, "fair," and less than 20%, "poor."

A typical fit[3] using the Brönsted catalysis law (1) is that for the mutarotation of glucose by thirteen carboxylate anions in water solution at 18°, where β = 0.36, $\underline{\epsilon}$ = 0.06 and $\underline{\Phi}$ = +77% ($\underline{n}$ = 13). This is a "good" fit, and is plotted in Fig. 1.

A typical fit using the Hammett equation 2 is that for the alkaline hydrolysis of twelve $\underline{m}$- and $\underline{p}$-substituted ethyl benzoates in 92% ethanol-8% water by volume at 30°, where ρ = +2.50, $\underline{\epsilon}$ = 0.06 and $\underline{\Phi}$ = 90% ($\underline{n}$ = 12). This fit is excellent, and is shown in Fig. 2.

A typical fit, with our equation 7 based on methyl bromide (for which $\underline{s}$ = 1.00) is that for various reactions of ethyl $\underline{p}$-toluenesulfonate in 39% water-61% dioxane at 50°, where $\underline{s}$ = 0.66, $\underline{\epsilon}$ = 0.15 and $\underline{\Phi}$ = 83% ($\underline{n}$ = 4).

BRONSTED PLOT

MUTAROTATION of GLUCOSE by RCOO⁻ Water, 18°

$\log k/k°$ Rate

$\log K_B/K_B°$ Ionization of RCOO⁻

R= Me₃C, MeCH₂, Me

ØCH₂

H, HOCH₂

Ø

o-MeC₆H₄

ØCHOH

β = 0.34

o-ClC₆H₄

ClCH₂

o-HOC₆H₄

CNCH₂

BRONSTED AND GUGGENHEIM 1927

HAMMETT PLOT

ALKALINE HYDROLYSIS of RCOOEt
92% EtOH by vol., 30°

ρ = 2.50

R =
p-NO₂C₆H₄
m-NO₂
m-Br
m-Cl
p-Br
p-Cl
p-F
m-MeO
Ø
m-Me
p-Me
p-MeOC₆H₄
ØCH₂
ØCH₂CH₂
Me
Et
Pr
o-FC₆H₄
o-Br
o-Cl
o-I

KINDLER 1926-36

σ = log Kₐ/Kₐ° Ionization of RCOOH in water, 25°

log k/k° Hydrolysis of Esters

The Grunwald-Winstein equation 3 with solvent parameters based on t-butyl chloride (for which $\underline{m}$ = 1.00) gives $\underline{m}$ = 0.87, $\underline{\epsilon}$ = 0.06, $\bar{\phi}$ = 92% ($\underline{n}$ = 7) for t-butyl bromide, $\underline{m}$ = 1.13, $\underline{\epsilon}$ = 0.57, $\bar{\phi}$ = 47% ($\underline{n}$ = 11) (Fig. 3); for benzhydryl chloride; $\underline{m}$ = 0.47, $\underline{\epsilon}$ = 0.90, $\bar{\phi}$ = 17% ($\underline{n}$ = 8) for trityl fluoride; $\underline{m}$ = 0.03, $\underline{\epsilon}$ = 0.38, $\underline{\phi}$ = 0% ($\underline{n}$ = 8) for n-butyl bromide; and $\underline{m}$ = 0.02, $\underline{\epsilon}$ = 1.35, $\bar{\phi}$ = 0% ($\underline{n}$ = 8) for p-nitrobenzoyl chloride.

The four-parameter equation 8 gives c_1 = 1.00, c_3 = 1.00, $\underline{\epsilon}$ = 0.25, $\bar{\phi}$ = 85% ($\underline{n}$ = 15) for t-butyl chloride; c_1 = 1.24, c_3 = 1.25, $\underline{\epsilon}$ = 0.19, $\underline{\phi}$ = 84% ($\underline{n}$ = 9) for benzhydryl chloride;[32] c_1 = 0.37, c_3 = 1.12,

(32) The number of points ($\underline{n}$) which equals the number of solvents serving to test the equation is generally one more for the equation 3 of Grunwald and Winstein than for equation 8 or equation 9 because with equation 3 the least squares line was not compelled to run through 80% ethanol; this gives equation 3 an additional point and slightly higher calculated ϕ values than if it had been treated similarly to equations 8 and 9. Benzhydryl chloride has only $\underline{n}$ = 9 for equation 8 because the datum for 100% methanol was not known to us when the Mark IV computation was carried out.

$\underline{\epsilon}$ = 0.25, $\underline{\phi}$ = 79% ($\underline{n}$ = 7) for trityl fluoride; c_1 = 0.80, c_3 = 0.27, $\underline{\epsilon}$ = 0.06, $\underline{\phi}$ = 93% ($\underline{n}$ = 5) for methyl bromide; c_1 = 0.77, c_2 = 0.34, $\underline{\epsilon}$ = 0.05, $\bar{\phi}$ = 89% ($\underline{n}$ = 7) for n-butyl bromide; c_1 = 0.81, c_2 = 0.52, $\underline{\epsilon}$ = 0.23, $\underline{\phi}$ = 72% ($\underline{n}$ = 12) for benzoyl chloride; c_1 = 1.36, c_3 = 0.66, $\underline{\epsilon}$ = 0.11, $\underline{\phi}$ = 91% ($\underline{n}$ = 9) for benzoyl fluoride; and c_1 = 1.09, c_3 = 0.21, $\underline{\epsilon}$ = 0.07, $\underline{\phi}$ = 95% ($\underline{n}$ = 7) for p-nitrobenzoyl chloride.

The special two-parameter equation 9 based on methyl bromide (for which $\underline{a}$ = 0.00) gives $\underline{a}$ = 1.00, $\underline{\epsilon}$ = 0.05, $\underline{\phi}$ = 96% ($\underline{n}$ = 14) for t-butyl chloride; $\underline{a}$ = 0.78, $\underline{\epsilon}$ = 0.35, $\bar{\phi}$ = 69% ($\underline{n}$ = 12) for benzhydryl chloride; $\underline{a}$ = 0.18, $\underline{\epsilon}$ = 0.16, $\underline{\phi}$ = 86% ($\underline{n}$ = 11) for n-butyl bromide; $\underline{a}$ = 0.06, $\underline{\epsilon}$ = 0.25, $\underline{\phi}$ = 68% ($\underline{n}$ = 11) for benzoyl chloride; $\underline{a}$ = -0.37, $\underline{\epsilon}$ = 0.12, $\bar{\phi}$ = 85% ($\underline{n}$ = 6) for p-nitrobenzoyl chloride; $\underline{a}$ = -0.04, $\underline{\epsilon}$ = 0.16, $\underline{\phi}$ = 59% ($\underline{n}$ = 7) for phenacyl bromide; and $\underline{a}$ = -0.42, $\underline{\epsilon}$ = 0.13, $\underline{\phi}$ = 46% ($\underline{n}$ = 7) for picryl chloride. These fits are especially remarkable

considering that no more parameters are being used than in equation 3, and only half as many as in the four-parameter equation 8.

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